

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 432 840 A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 90203215.0

(51) Int. Cl.⁵: **G01N 27/416**

(22) Date of filing: 06.12.90

(30) Priority: 12.12.89 IT 2266389

(43) Date of publication of application:
19.06.91 Bulletin 91/25

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR LI LU NL SE

(71) Applicant: **ENIRICERCHE S.p.A.**
Corso Venezia 16
I-20121 Milan(IT)

Applicant: **SNAM S.p.A.**
Corso Venezia 16
I-20121 Milan(IT)

(72) Inventor: **Alberti, Giulio**
Via Ruggero Torelli 67
I-06100 Perugia(IT)
Inventor: **Casciola, Mario**
Via Vailati 1
I-06100 Perugia(IT)
Inventor: **Palombari, Roberto**
Strada Bagnoli Gioco 1
I-06100 Perugia(IT)

(74) Representative: **Roggero, Sergio et al**
Ing. Barzanò & Zanardo Milano S.p.A. Via
Borgonuovo 10
I-20121 Milano(IT)

(54) **Solid-state sensor for the determination of the concentration of gases which can react with hydrogen.**

(57) A solid-state sensor for determining the concentration of gases which can react with hydrogen, in particular, of oxygen, is disclosed, which is essentially constituted by a solid-state proton conductor into contact: on the one side, with a reference electrode, constituted in its turn by a metal hydride or a metal alloy, and on the other side with an electrode which catalyses the reaction of the gas to be detected, with said sensor being connected with a power feed system which supplies current or voltage impulses, and with a system which detects the value of potential after each impulse.

EP 0 432 840 A2

"SOLID-STATE SENSOR FOR THE DETERMINATION OF THE CONCENTRATION OF GASES WHICH CAN REACT WITH HYDROGEN"

The present invention relates to a solid-state sensor for determining the concentration of gas species, in particular oxygen, which can react with hydrogen, which solid-state sensor can also operate at room temperature.

The determination of the oxygen content in a gas mixture or in liquids is an important problem from the industrial, biological, environmental, and still other, view points.

Very often, a continuous monitoring is required, as in rivers, lakes or seas, to keep controlled the level of pollution caused by organic materials. Such a requirement can also occur in case of biological liquids in general, or in gases generated by combustion processes, and other processes.

For that purpose, a method of voltammetric type (Clark's method) is used [see: M. Kleitz, A. Pelloux, M. Gauthier in "Fast Ion Transport in Solids", page 69, Elsevier North Holland, Inc. (1979)].

During the past ten years, also potentiometric systems were introduced, which use a solid conductor for O₂, usually zirconium oxide doped with yttrium, which anyway operate successfully only at temperatures higher than 400-500 °C [see: E. Siebert, J. Fouletier, S. Vilminot "Solid State Ionics", 9 & 10 (1983) 1291].

Recently, attempts were carried out aiming at lowering the operating temperature of the potentiometric sensors, by studying other types of solid electrolytes [see: N. Miura, J. Hisamoto, S. Kuwata, N. Yamazoe "Chemistry Letters" (1987) 1477; T. Inoue, K. Eguchi, H. Arai "Chemistry Letters" (1988) 1939; S. Kuwata, N. Miura, Y. Yamazoe "Chemistry Letters" (1988) 1197].

The present Applicant surprisingly found now a new sensor which makes it possible, also operating at room temperature, to detect those gases which react with hydrogen, by detaching the production of hydrogen on the sensor electrode.

The solid-state sensor according to the present invention, for determining the concentration of gases which can react with hydrogen, in particular oxygen, is essentially constituted by a solid-state proton conductor into contact: on the one side, with a reference electrode, constituted in its turn by a metal hydride or a metal alloy, and on the other side with a metal which catalyzes the reaction with hydrogen of the gas to be detected, with said sensor being connected with a power feed system which supplies current or voltage impulses, and with a system which detects the value of potential after each impulse.

As the proton conductor, one already known from literature can be used such as, e.g., uranyl hydrogen phosphate, antimonic acid, phosphomolibdic acid, zirconium hydrogen phosphate, zirconium triphosphate and its forms doped with silicates, such as H₃Zr₂PO₄ (SiO₄)₂ and organic polymers containing acidic groups, such as -COOH, -SO₃ (for example, NAFION or IONAC membranes).

Zirconium hydrogen phosphate may preferably be used in film or membrane form, as disclosed in European Patent Application Publication N.330248.

The coating of the reference electrode with such films or membrane can be carried out as disclosed in above said patent application.

Since very thin, compact films (thickness lower than 0.1 mm) can be obtained, the electrical resistance of the system is appreciably reduced. Furthermore, such a proton conductor is suitable for uses at room temperature and at higher then room temperatures, up to a maximum value of 350-400 °C, beyond which the acidic groups

-P-OH

condense to yield pyrophosphate.

As reference electrodes, various metals, or metal alloys can be used, which form hydrides. Titanium and zirconium hydrides are preferred. Owing to the low conductivity of zirconium hydride at room temperature, said hydride should be preferably used at temperatures higher 100 °C by electrolytic way.

The reference electrode of titanium or zirconium hydride can be prepared, e.g., by heating at temperatures comprised within the range of from 400 to 700 °C and for a time of from 2 to 10 hours, a titanium or zirconium sheet (having a thickness of from 0.25 to 1.0 mm) in the presence of hydrogen gas as disclosed in European Patent Appln. Publ. N.330248. The production can be carried out by electrolytic route as well.

As catalyzing electrodes, the metals known from the prior art can be used. Among them, platinum and palladium are preferred. The electrode is preferably given the shape of a net or of a thin wire (0.1-0.5 mm) wound to give a flat and thin spiral. Also a platinum-coated metal can be used, on condition that the surface is not excessively porous.

The sensor may be completed with an auxiliary electrode to which the pulsed current or the pulsed voltage is applied.

In such a way, one can prevent the pulsed current from also flowing through the reference electrode.

The auxiliary electrode can be constituted by a metal hydride and such a hydride can be the same as used for the reference electrode: titanium hydride and zirconium hydride are preferred.

From a theoretical view point, the auxiliary electrode is liable to lose its hydrogen content during sensor operation.

On considering that through such an electrode extremely small current amounts flow, compared to the amount of hydrogen contained in the metal hydride, no drawbacks are expected to occur even after several years of operation.

If through the feed circuit a pulsed current flows, the impulse length can be of the order of from 10 to 100 milliseconds, while the time interval between two consecutive impulses can be of the order of from 1 to 10 seconds. During the application of an impulse, the auxiliary electrode operates as the anode. The hydrogen contained in the metal hydride flows through the proton conductor as H^+ and an equivalent amount of protons is reduced at the catalyzing electrode, which operates as the cathode. The used current can be of the order of from 0.1 to 1.0 microamperes, depending on the surface-area of the electrode used.

The width of the impulse is kept constant.

The potential of the sensor is determined after each current impulse. It is of course pulsed, and therefore can be filtered or, even better, it can be measured during a short time, of the order of one second, for example by a sample-hold system, before the successive impulse is applied.

The present Applicant found that the measured potential value is a function of O_2 partial pressure according to the following equation:

$$E = a + b \log P_{O_2} \quad (1)$$

in which:

a is a constant depending on the reference potential and on the operating conditions, such as current intensity, impulse frequency, and so on;

b is a constant of the order of 100 mV, influenced by the operating conditions as well.

The range of validity of equation (1) was determined by performing exponential dilutions of air in a stream of nitrogen flowing at a constant flow rate. A linear behaviour was found to exist down to concentrations of O_2 of the order of some parts per million parts,

In Figure 1 a sensor with an auxiliary electrode is schematically shown. In the figure:

C_a = pulsed-power feed circuit

C_m = measurement circuit

E_c = catalyzing electrode

E_r = reference electrode

E_a = auxiliary electrode

C_p = proton conductor.

Some examples are given now, the purpose of which is of better illustrating the present invention. In no way shall such examples be construed as being limitative of the same invention.

Examples

Example 1

A sensor constituted by: zirconium phosphate in film form (thickness 0.1 mm) as the proton conductor, titanium hydride as the reference electrode and platinum as the catalyzing electrode, operating under the following experimental conditions: temperature $20^\circ C$, feed with current impulses of 1 microampere, of 100 milliseconds of length and with a period of 10 seconds, measurements of potential carried out with a delay of 8 s after the impulse, was used to measure the content of O_2 in air and in nitrogen-air mixtures with a relative humidity close to 100%.

The results, reported in the chart of Figure 2, show the response reproducibility and velocity of the sensor at various partial pressures of O_2 (indicated in the figure).

Example 2

A sensor according to Example 1, operating under the same experimental conditions except current being of 0.5 microamperes, was used to measure the content of oxygen in oxygen-nitrogen mixtures.

For that purpose, an exponential-dilution system was used; oxygen, contained at the initial concentration

C_0 inside a vessel of known volume V , was diluted by nitrogen fed at a constant flow-rate F . Oxygen leaves the vessel at a concentration C depending on time according to the equation

$$\ln C = \ln C_0 - Ft/V$$

Since the potential depends on O_2 concentration according to a logarithmic relation, one should expect a linear decrease of potential with time.

Figure 3 shows the response of the sensor with varying times and varying oxygen concentrations (the numerical values reported in the figure are the logarithm of O_2 partial pressures). The potential decrease is in perfect agreement with the expected trend.

10 Example 3

A sensor according to Example 1, operating under the following experimental conditions: temperature 40°C , impulsive current 0.3 microamperes, impulse lengths of 10 milliseconds, period 10 s, potential measurement delay 8 seconds, was used to measure the content of O_2 in mixtures with nitrogen, by the exponential-dilution system.

The response of the sensor to O_2 concentrations over time is reported in Figure 4 (the numerical values reported in the figure are the logarithm of O_2 partial pressures).

Example 4

20

A sensor according to Example 1, but of the double-electrode type, i.e., equipped with a TiH_x blade acting as the reference electrode-auxiliary electrode, was tested at 80°C with humidified gases at room temperature.

The operating conditions were: current of 0.10 microamperes, impulse length of 10 milliseconds, period of 10 seconds, potential measurement delay 8 seconds. The response of the sensor as a function of time and of the partial pressure of O_2 , obtained by exponential dilution, is illustrated in Figure 5.

Example 5

30 A sensor analogous to that of Example 1, except the proton conductor being constituted by a membrane of NAFION (of 0.1 mm of thickness) operating under the experimental conditions of Example 1 except current intensity, which was of 0.3 microamperes, was used to measure the content of O_2 in mixtures with nitrogen.

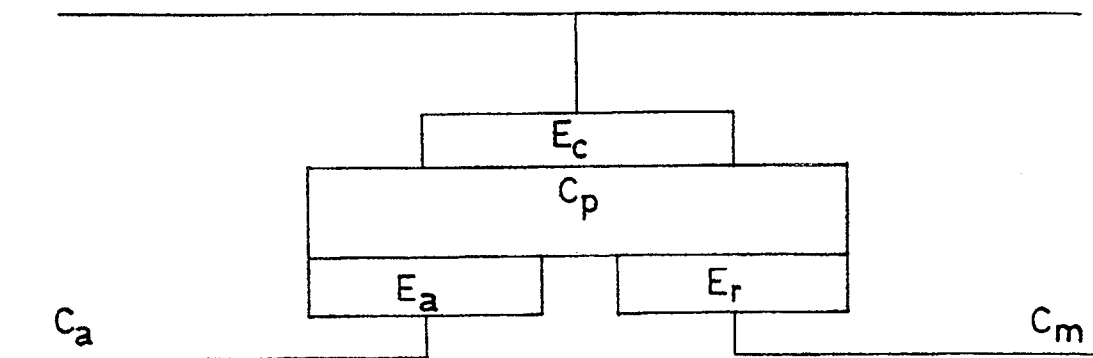
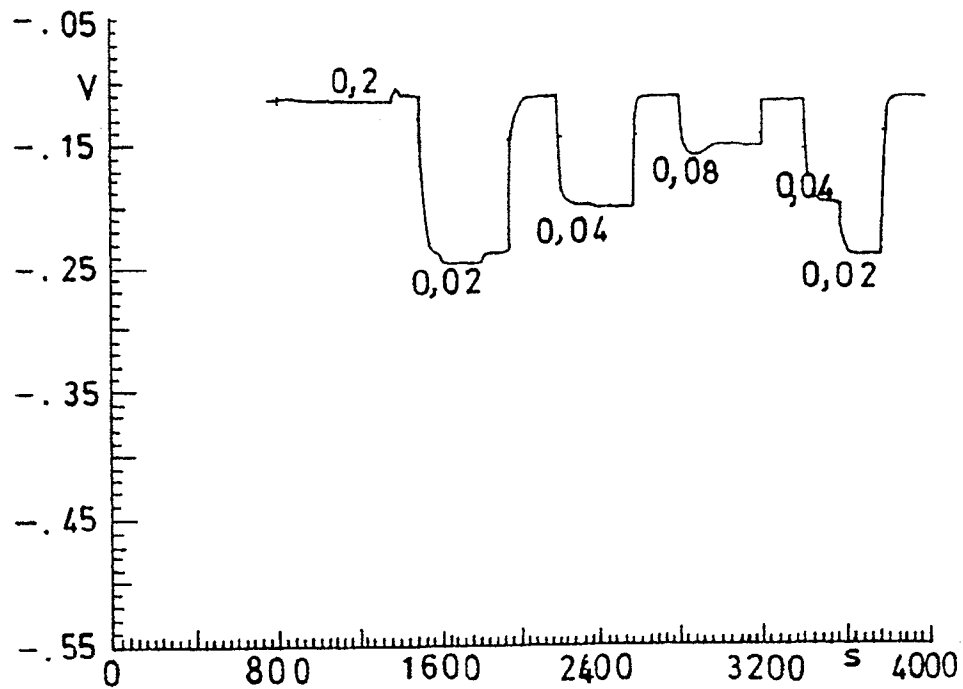
The chart reported in Figure 6 shows the dependence of the potential reading on the logarithm of the partial pressure of O_2 .

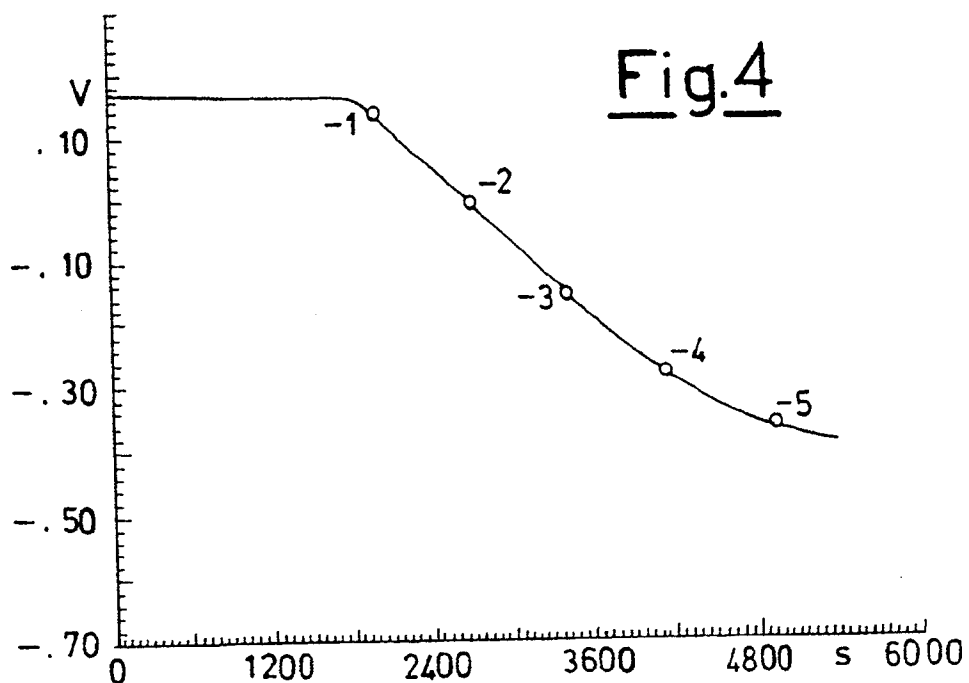
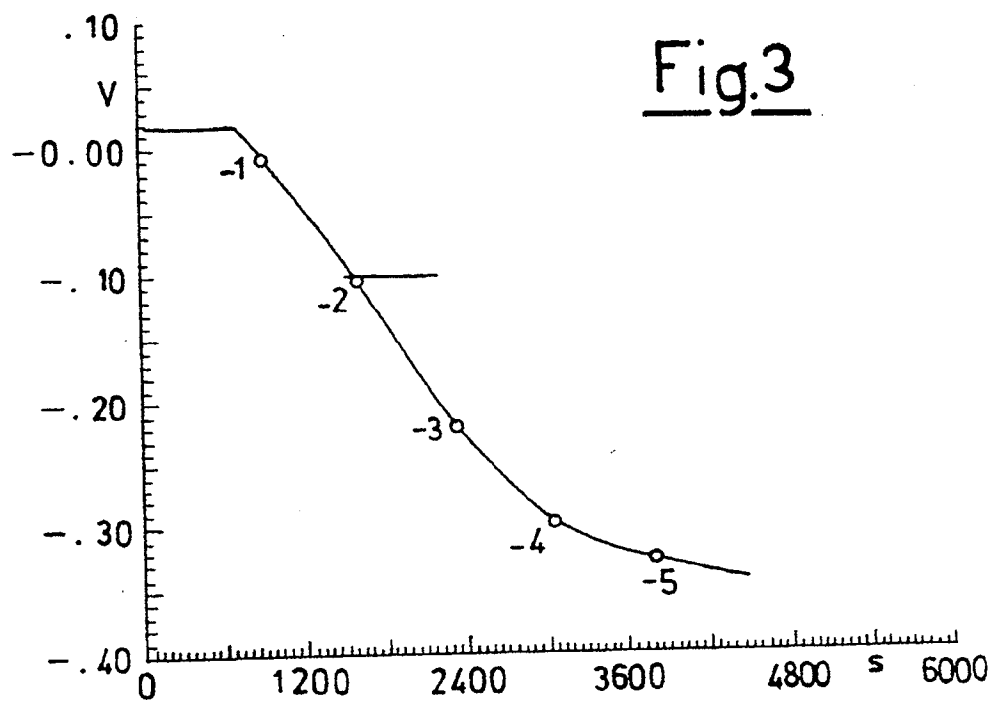
Claims

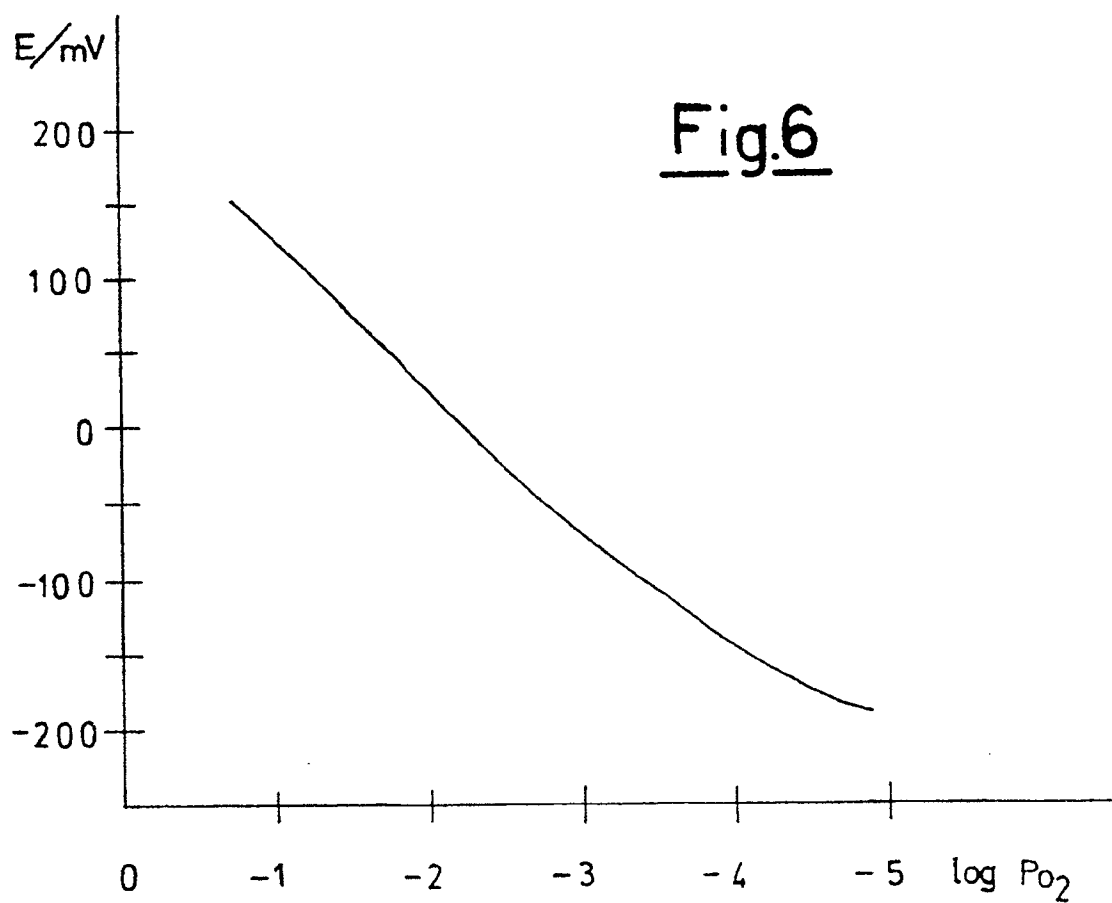
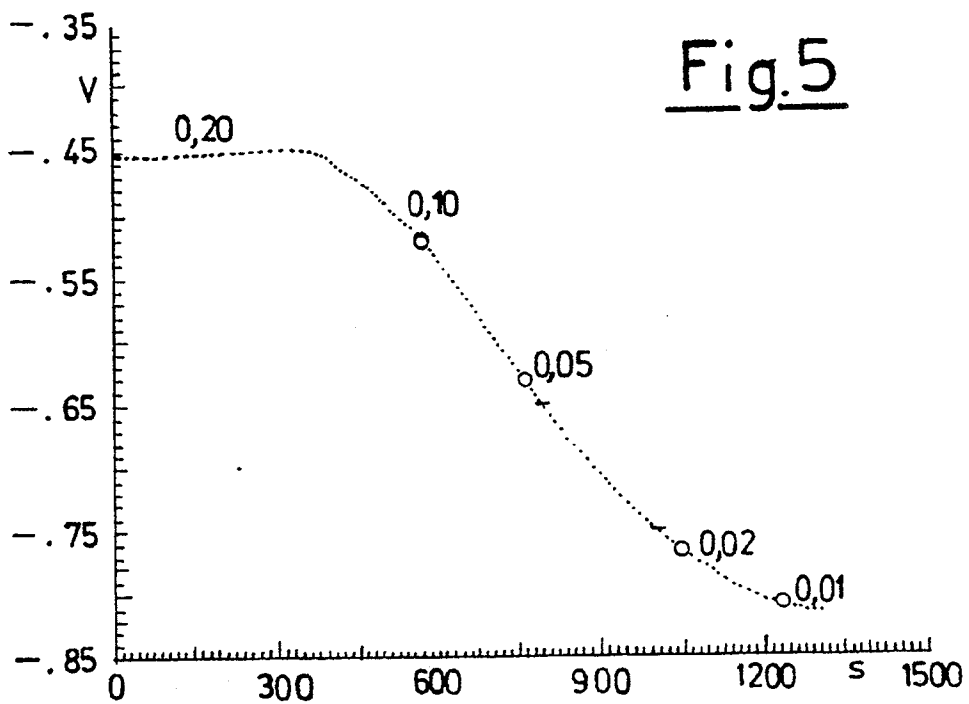
- 40 1. Solid-state sensor for determining the concentration of gases which can react with hydrogen, in particular of oxygen, essentially constituted by a solid-state proton conductor into contact: on the one side, with a reference electrode, constituted in its turn by a metal hydride or a metal alloy, and on the other side with an electrode which catalyzes the reaction with hydrogen of the gas to be detected, with said sensor being connected with a pulse feed system which supplies current or voltage impulses, and with a system which detects the value of potential after each impulse.
- 45 2. Sensor according to claim 1, in which the solid-state conductor for protons is selected from the group consisting of uranyl hydrogen phosphate, antimonous acid, phosphomolibdic acid, zirconium hydrogen phosphate and the organic polymers containing acidic groups.
- 50 3. Sensor according to claim 2, in which the zirconium hydrogen phosphate is in film or membrane form.
4. Sensor according to claim 1, in which the reference electrode is selected from titanium hydride and zirconium hydride.
- 55 5. Sensor according to claim 1, in which the catalyzing electrode is a noble metal.
6. Sensor according to claim 5, in which the noble metal of the catalyzing electrode is selected from

platinum and palladium.

7. Sensor according to claim 1, in which also an auxiliary electrode is present, to which the current or voltage impulses are fed by the power feed system.
8. Sensor according to claim 7, in which the auxiliary electrode is a metal hydride or a metal alloy.
9. Sensor according to claim 8, in which the hydride of the auxiliary electrode is selected from titanium hydride and zirconium hydride.

Fig.1Fig.2





(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 432 840 A3

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 90203215.0

(51) Int. Cl.⁵: G01N 27/416, G01N 27/56

(22) Date of filing: 06.12.90

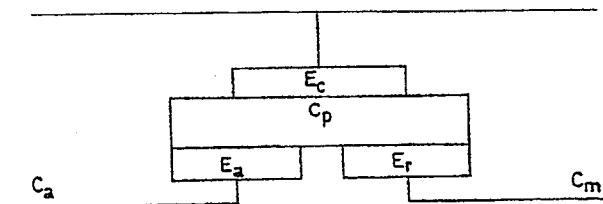
(30) Priority: 12.12.89 IT 2266389

(43) Date of publication of application:
19.06.91 Bulletin 91/25(64) Designated Contracting States:
AT BE CH DE DK ES FR GB GR LI LU NL SE(68) Date of deferred publication of the search report:
25.09.91 Bulletin 91/39(71) Applicant: ENIRICERCHE S.p.A.
Corso Venezia 16
I-20121 Milan(IT)Applicant: SNAM S.p.A.
Corso Venezia 16
I-20121 Milan(IT)(72) Inventor: Alberti, Giulio
Via Ruggero Torelli 67
I-06100 Perugia(IT)
Inventor: Casciola, Mario
Via Vailati 1
I-06100 Perugia(IT)
Inventor: Palombari, Roberto
Strada Bagnoli Gioco 1
I-06100 Perugia(IT)(74) Representative: Roggero, Sergio et al
Ing. Barzanò & Zanardo Milano S.p.A. Via
Borgonuovo 10
I-20121 Milano(IT)

(54) Solid-state sensor for the determination of the concentration of gases which can react with hydrogen.

(57) A solid-state sensor for determining the concentration of gases which can react with hydrogen, in particular, of oxygen, is disclosed, which is essentially constituted by a solid-state proton conductor into contact: on the one side, with a reference electrode, constituted in its turn by a metal hydride or a

metal alloy, and on the other side with an electrode which catalyses the reaction of the gas to be detected, with said sensor being connected with a power feed system which supplies current or voltage impulses, and with a system which detects the value of potential after each impulse.

Fig.1

EP 0 432 840 A3



EUROPEAN SEARCH REPORT

EP 90 20 3215

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 231 766 (FIGARO ENGINEERING) * Abstract; page 9, lines 9-15; page 10, lines 13-21; page 11, lines 4-9; figures 1-5,8 * - - - -	1,2,4-6	G 01 N 27/416
Y	PATENT ABSTRACTS OF JAPAN, vol. 5, no. 182 (P-90)[854], 20th November 1981; & JP-A-56 111 453 (MATSUSHITA) 03-09-1981 * Whole document * - - - -	1,2,4-6	
A	SOLID STATE IONICS, vol. 35, no. 1/2, July/August 1989, pages 153-156; G. ALBERTI et al.: "All solid state hydrogen sensors based on pellicular α -zirconium phosphate as a protonic conductor" * Pages 153,154 * - - - -	1-6	
A	EP-A-0 060 944 (WESTINGHOUSE) * Abstract * - - - -	1	
A	EP-A-0 107 279 (HITACHI) * Abstract; claims 1,4; figure 1 * - - - - -	1,2,5,6	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G 01 N
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		06 June 91	KEMPF G.V.
CATEGORY OF CITED DOCUMENTS			
X: particularly relevant if taken alone		E: earlier patent document, but published on, or after the filing date	
Y: particularly relevant if combined with another document of the same category		D: document cited in the application	
A: technological background		L: document cited for other reasons	
O: non-written disclosure			
P: intermediate document		&: member of the same patent family, corresponding document	
T: theory or principle underlying the invention			